Ethylene Dibromide at UST sites?

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SC UST Program

- SC is highly dependent on groundwater as a source of drinking water
- First UST regulations promulgated 1985
- SUPERB program implemented 1988
- Risk-Based Corrective Action (RBCA) approach implemented 1994

RBCA – identify chemicals of concern

- EDB is Toxic – MCL set at 0.05 µg/l (suspected carcinogen : 2 x 10^{-6} risk factor)
- EDB is mobile (impact to water supply wells at about 3% of facilities in SC with confirmed EDB)
- EDB is persistent through time (>25 years) and space (large plumes)

Ethylene Dibromide (EDB or 1,2-Dibromoethane)

- $C_2H_4Br_2$
- Synthetic halogenated organic chemical
- Used as a soil fumigant from ~1950’s - 1983
- Used in gasoline from ~1920’s – 1980’s as a lead-based antiknock additive

Chemical Properties of EDB

Property	Benzene	MTBE	EDB
Aqueous solubility	1750 mg/l	51,260 mg/l	4,321 mg/l
Vapor pressure	8.00 kPa	32.62 kPa	1.47 kPa
Koc	83.0 l/kg	12.3 l/kg	44.0 l/kg
Henry's constant	0.22	0.023	0.029
retardation, Foc= .001	1.31	1.05	1.17
retardation, Foc= .01	4.11	1.46	2.65

(Transport Properties from Falta, 2004b)

Breakdown of EDB

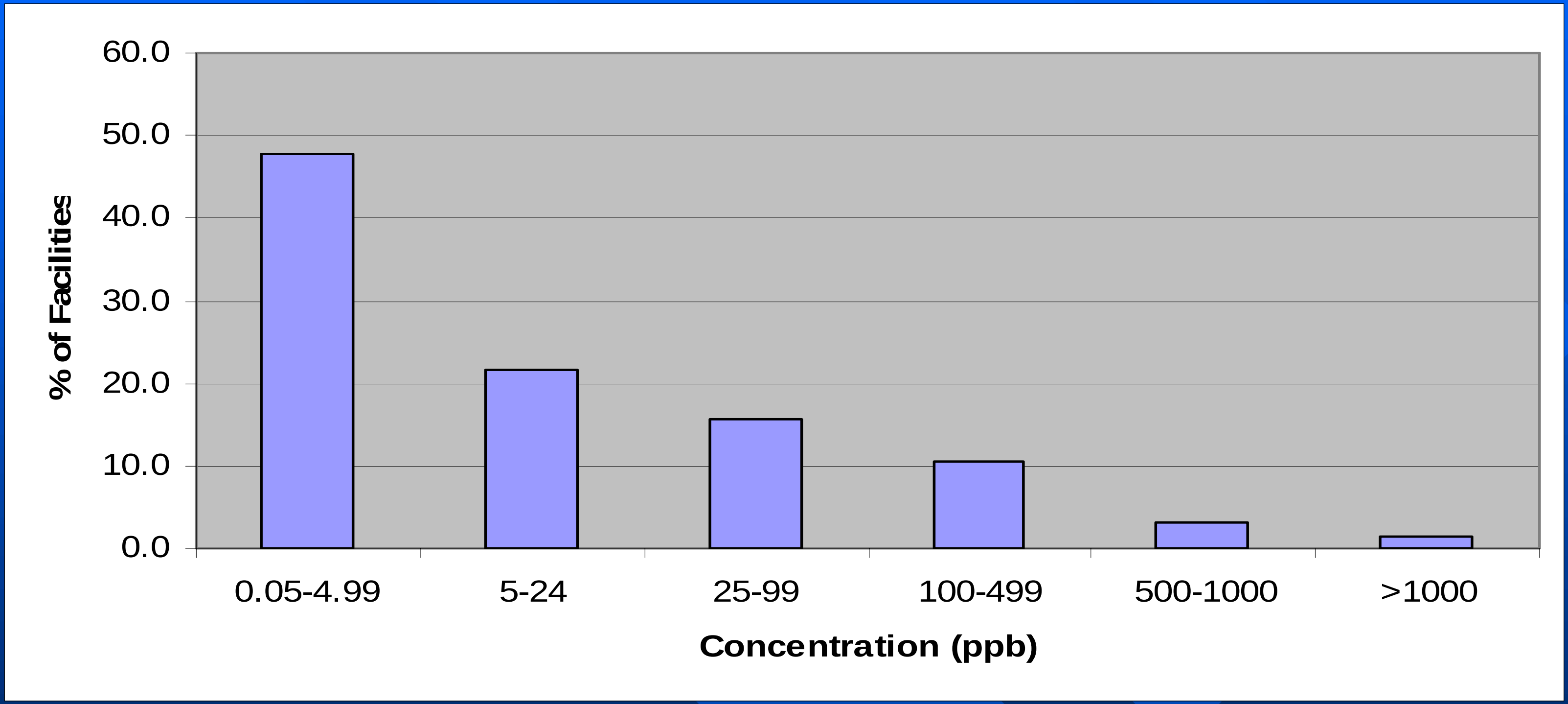
USGS Water Supply Paper 2402 (1993)

- Chemical Hydrolysis – 4 studies show half-lives from 1.5 – 15 years; by-products ethylene glycol and bromide ion
- Microbial Degradation – both aerobic and anaerobic degradation documented- half-lives from 35 to 350 days
- Nucleophilic substitution – EDB transformation enhanced by H_2S and HS^- ; by-products ethyl mercaptan, diethyl disulfide, triethyl disulfide

SC Background

- Sampling since early 1990s
- Initially used 8260B – Reporting limit 5 µg/l
- Later used 8011 – Reporting limit 0.02 µg/l
- EDB found at ~ 50% of assessed releases

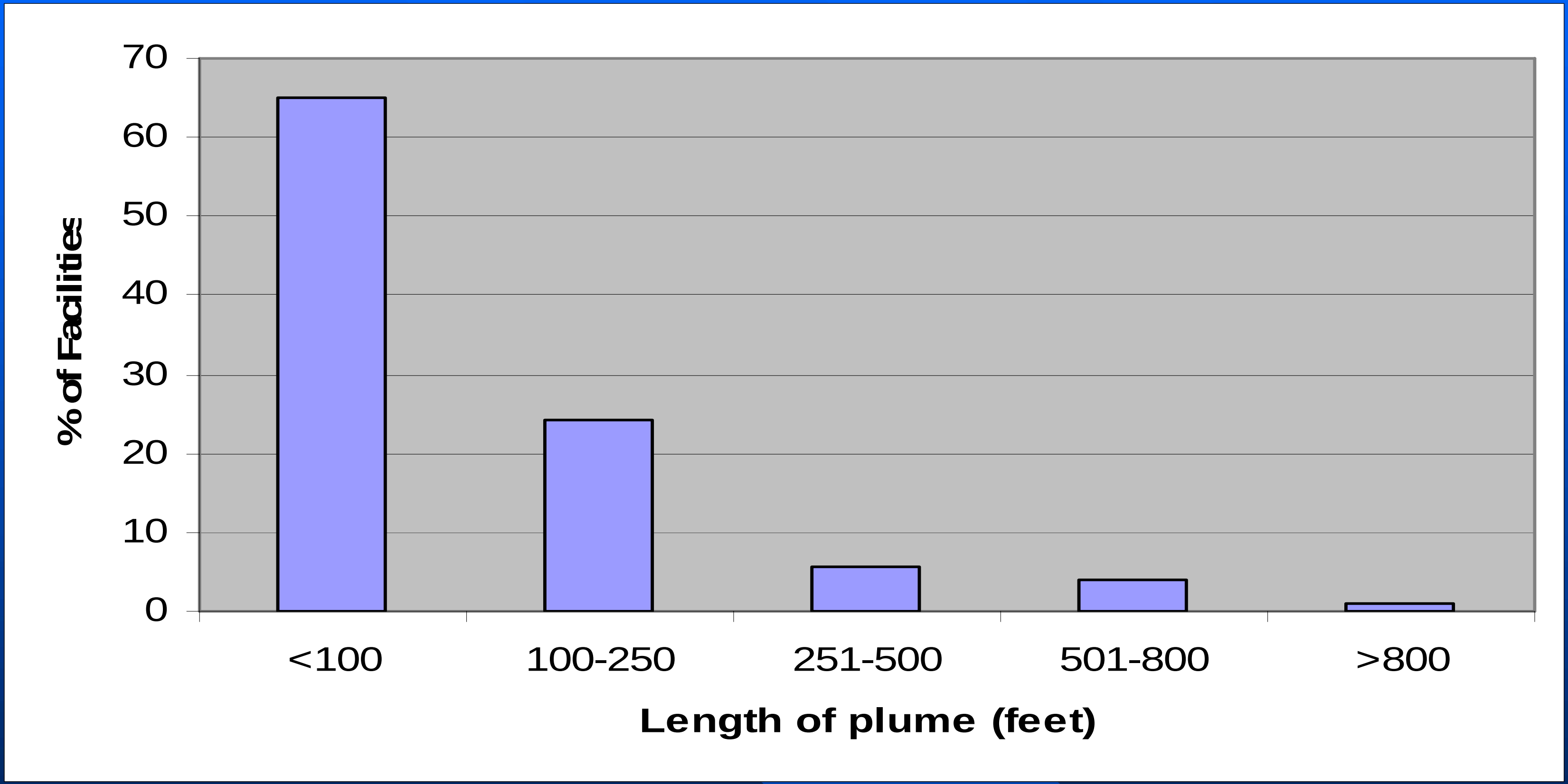
EDB Presence in SC



48% 21% 16% 11% 3% 1%

- Highest EDB concentration usually near or down from USTs
- Highest EDB concentration detected to date 6,600 µg/l

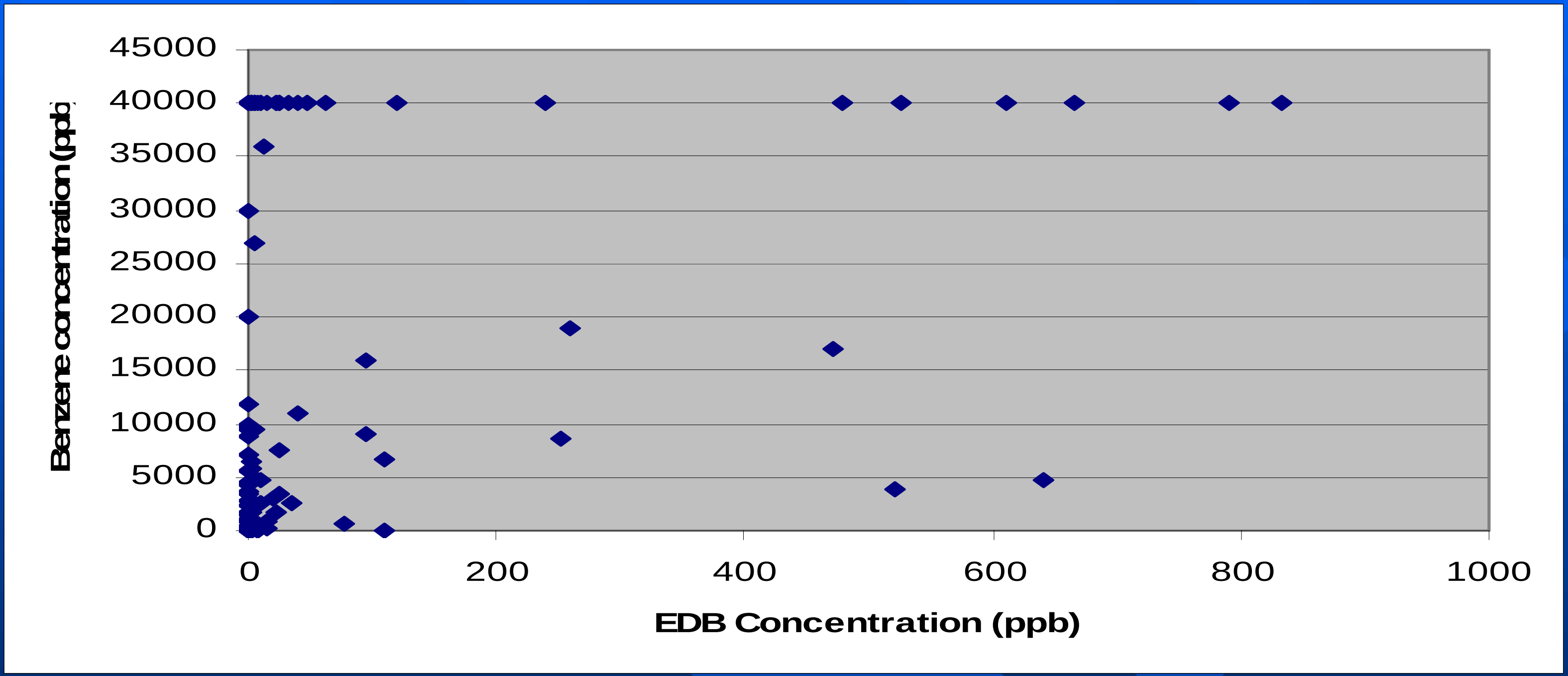
Length of EDB plumes in SC



Approximately 13% of EDB plumes exceed 250 feet length

The longest known UST related EDB plume in SC is 2,800 ft

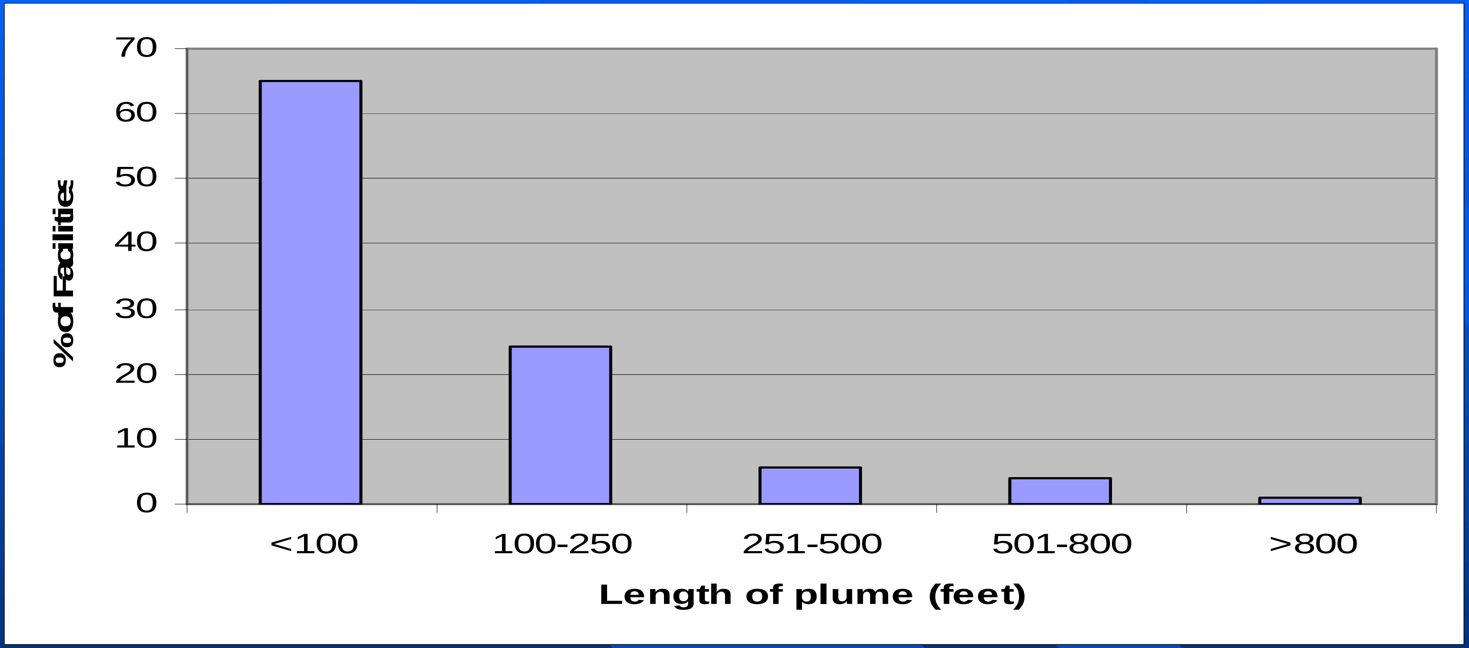
Benzene vs EDB Concentrations



There is no apparent correlation between the Benzene and EDB concentrations

Complicated by presence of multiple releases

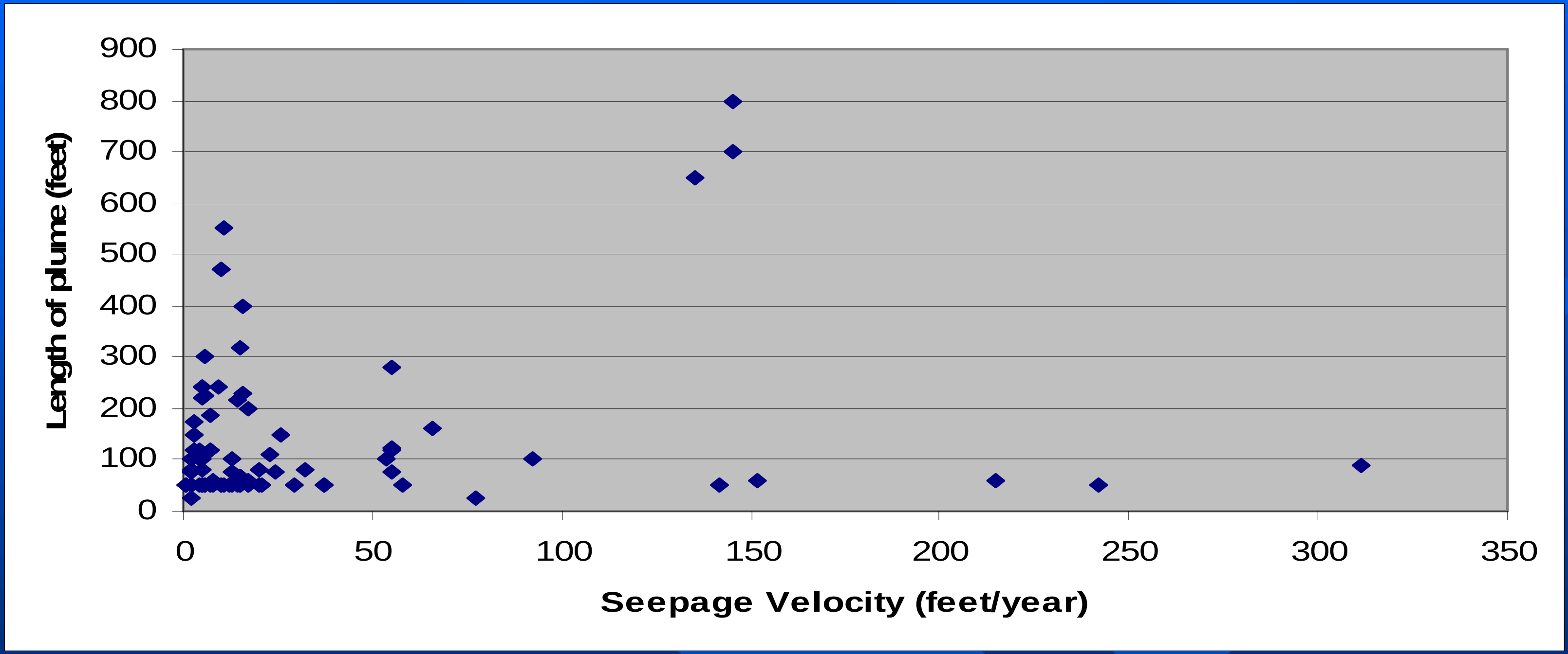
Length of EDB plumes in SC



Approximately 13% of EDB plumes exceed 250 feet length

Largest EDB plume found so far is 2,800 feet long

Plume Length vs Seepage Velocity



Other factors such as sorption or degradation may be affecting the plume length

EDB Distribution

- The longer EDB plumes tend to be narrow cigar-shaped bodies.
- Many EDB plumes dive with distance from source (please see the presentation after lunch on April 4 regarding diving plumes).
- In some cases, EDB is found in the deep monitoring wells but not in shallow water table wells.

EDB Assessment Challenges

- Looking for EDB at low concentrations (<100 ppb at 85% of sites)
- Current real-time field screening methods are not designed to look for EDB.
- Narrow linear EDB plumes may be missed by monitoring well network.
- 3-dimensional assessments needed to identify diving plumes

So we found EDB, what do we do about it?

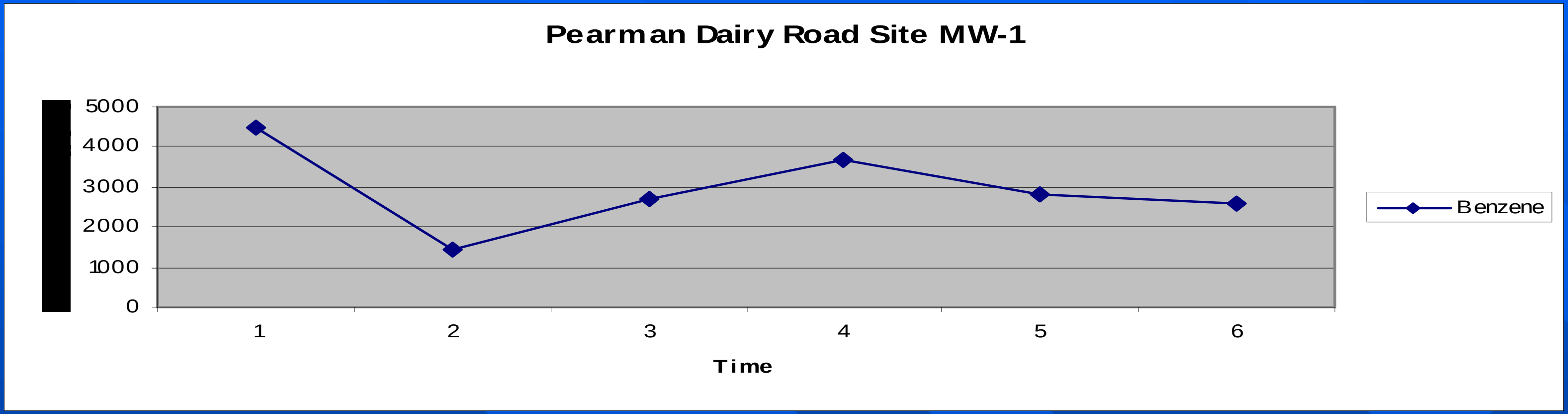
Risk-Based Corrective Action

- Identify receptors (wells, lakes, streams)
- Calculate Site-Specific Target Levels (clean-up goals) for each chemical to protect receptors
- If no risk, consider monitored natural attenuation
- If unacceptable risk, corrective action is necessary

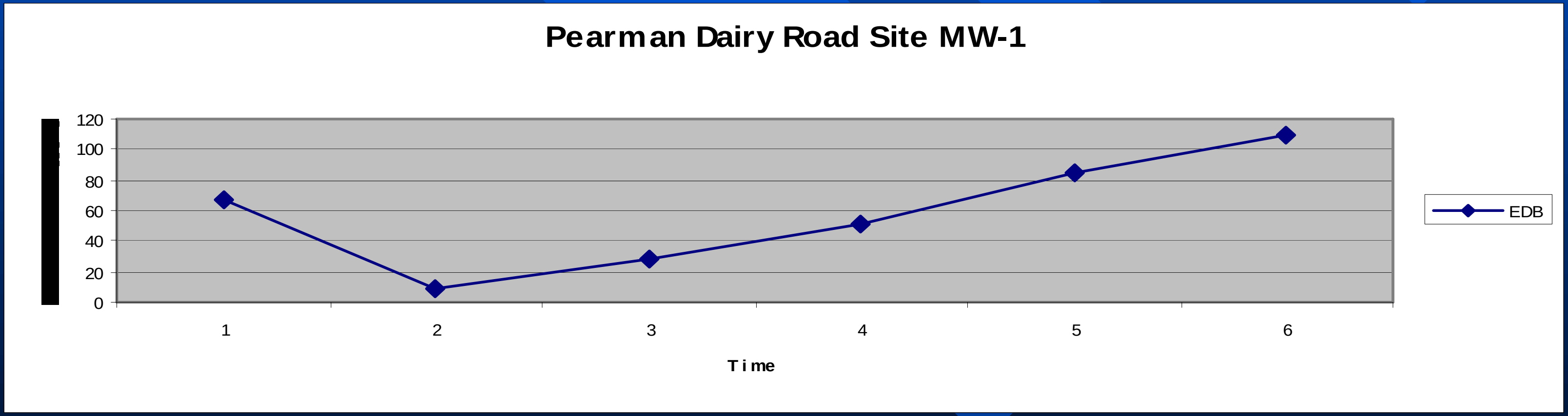
Natural Attenuation of EDB

- EDB is found on many sites even though it hasn't been used for 25 years
- EDB is more persistent than Benzene
- Some wells show temporal decreases in EDB concentration while other wells increase with time

MNA Example



Pearman Dairy Road Site MW-1
5000
4000
3000
2000
1000
0
1
2
3
4
5
6
Time
Benzene



Pearman Dairy Road Site MW-1
120
100
80
60
40
20
0
1
2
3
4
5
6
Time
EDB

Remediation of EDB

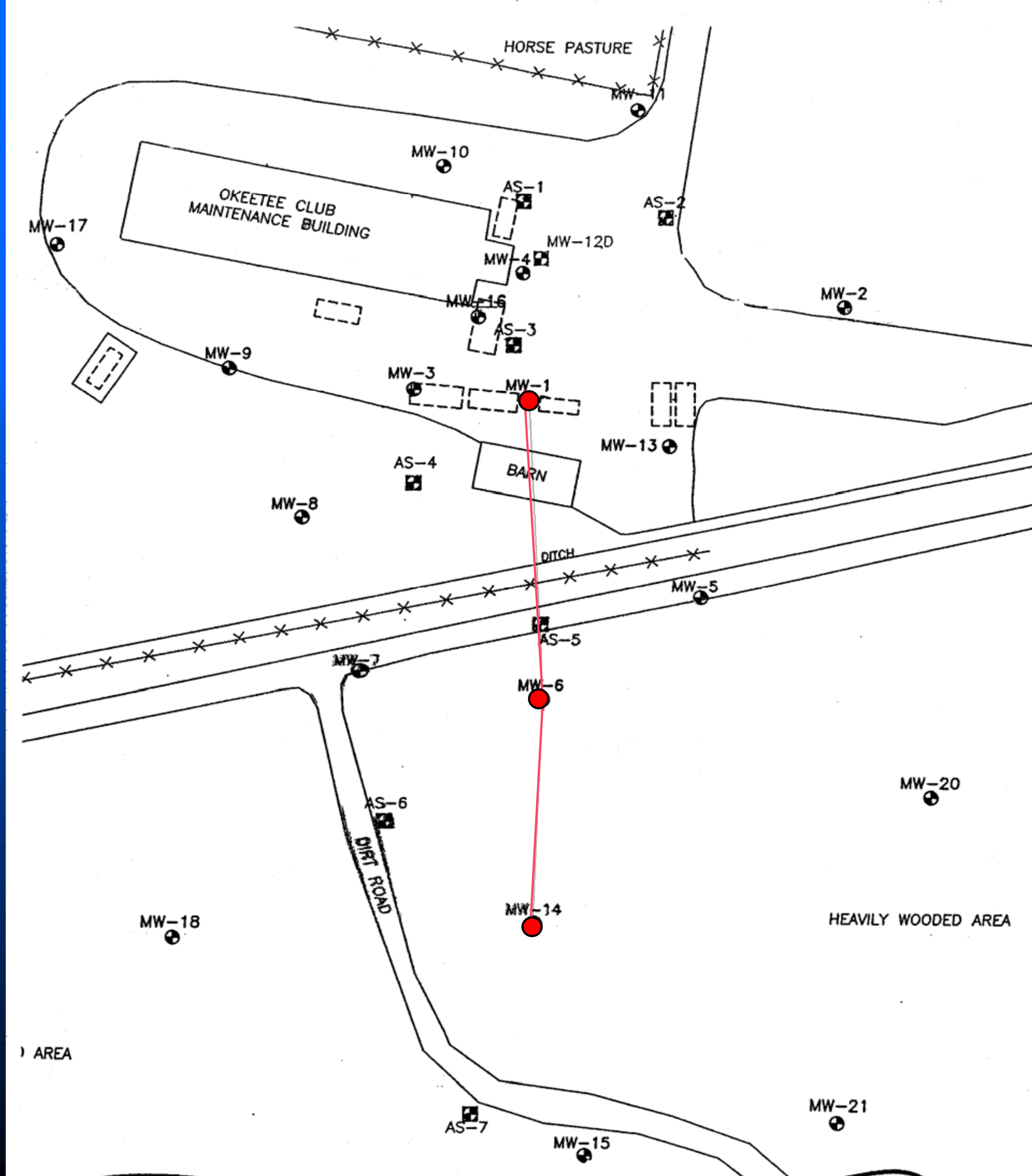
- Cleanup firms are directed to treat the EDB in cases where an impact to a receptor has or may occur
- Currently ~ 6% of UST cleanups in SC require treatment of EDB

Corrective Action Methods

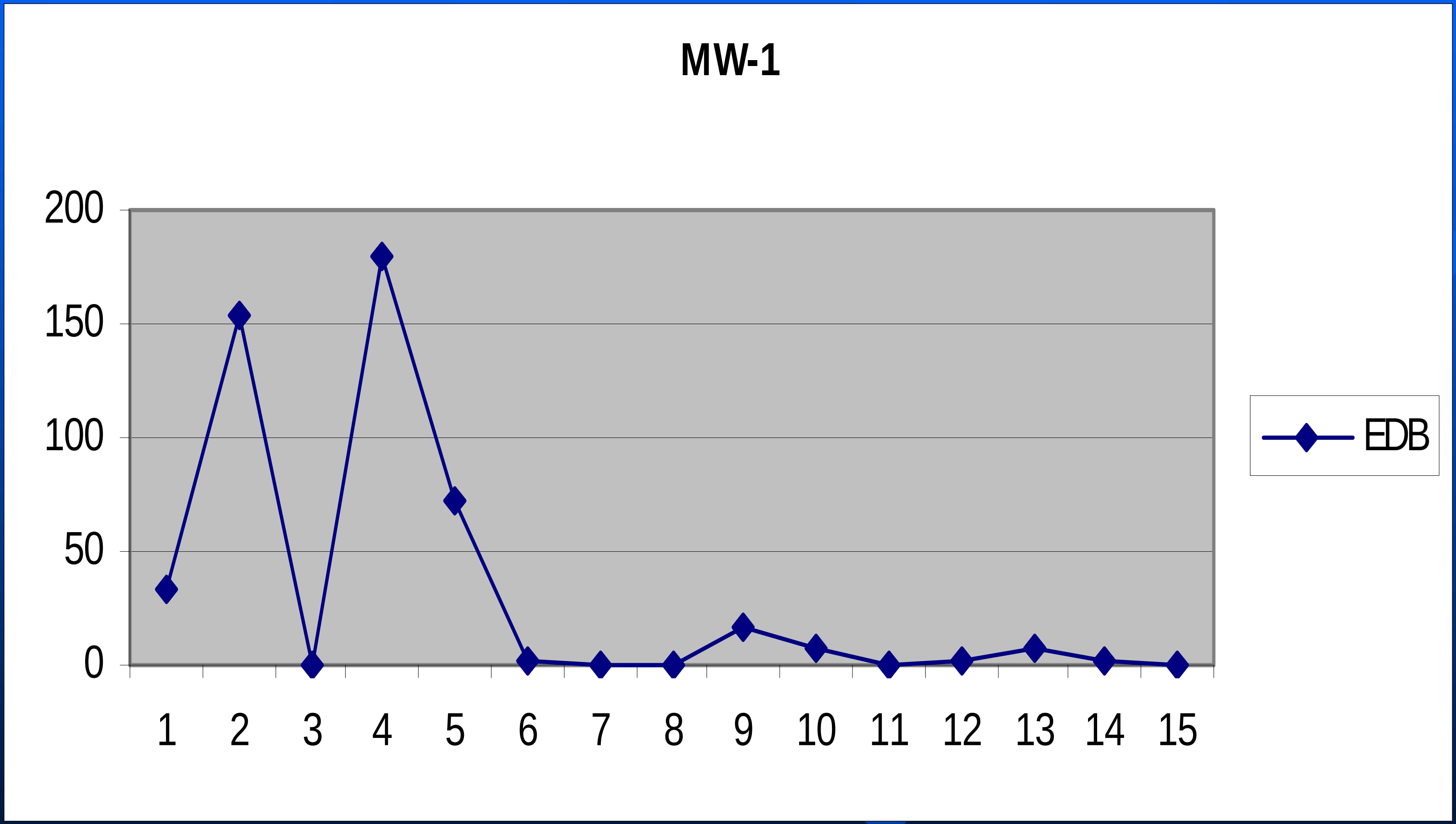
- Air Sparging
- Chemical Oxidation (e.g.,Hydrogen Peroxide)
- Bioremediation
- Phoster II™
- Pump and Treat

Air Sparging

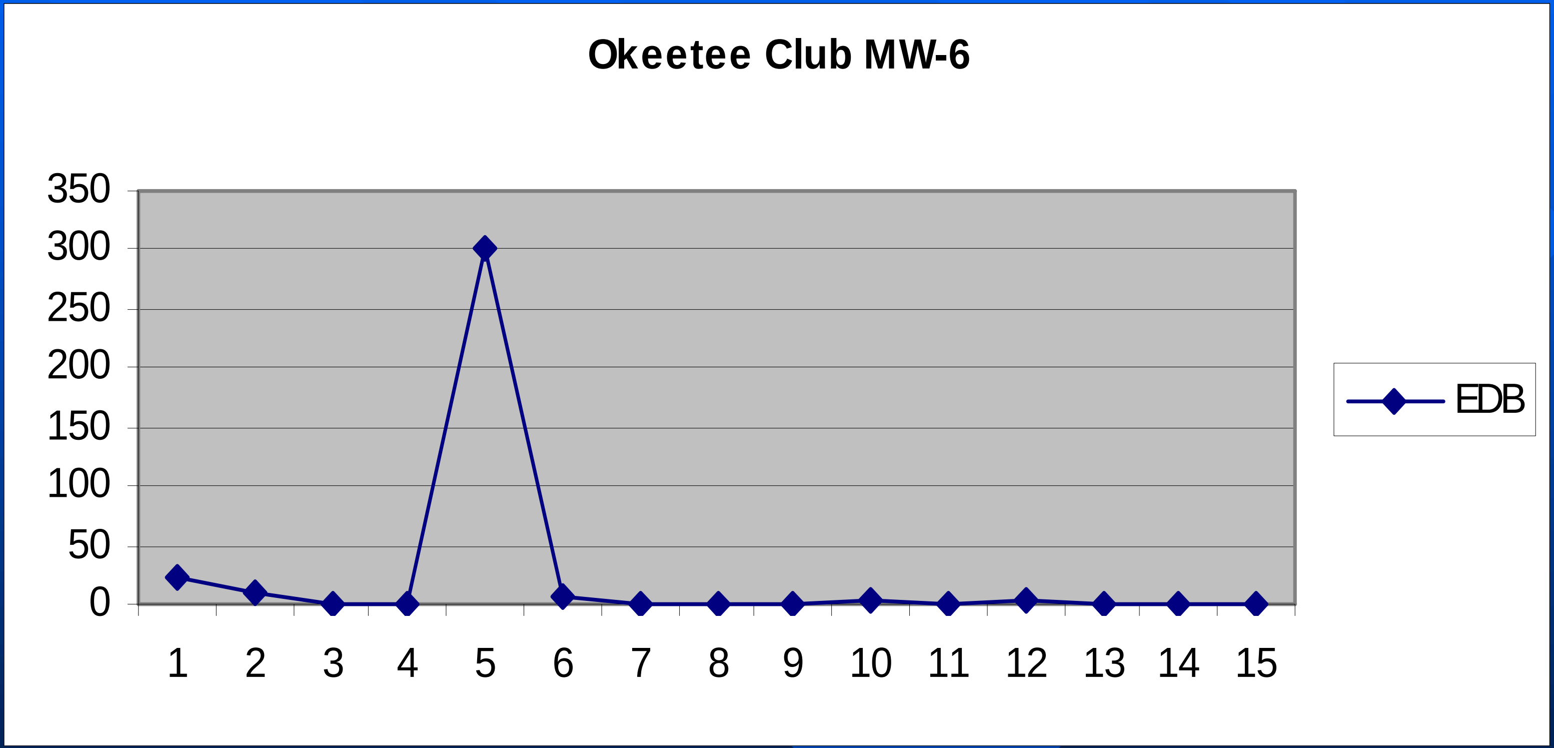
- Injection of ambient air beneath the water table interface to 1) enhance volatilization and 2) increase the oxygen concentration in order to also enhance aerobic bioremediation


HORSE PASTURE
MW-11
MW-10
AS-1
AS-2
OKEETEE CLUB
MAINTENANCE BUILDING
MW-17
MW-12D
MW-4
MW-2
MW-16
AS-3
MW-9
MW-3
MW-1
MW-13
AS-4
BARN
MW-8
DITCH
MW-5
AS-5
MW-7
MW-6
MW-20
AS-6
DIRT ROAD
MW-14
MW-18
HEAVILY WOODED AREA
AREA
MW-21
AS-7
MW-15

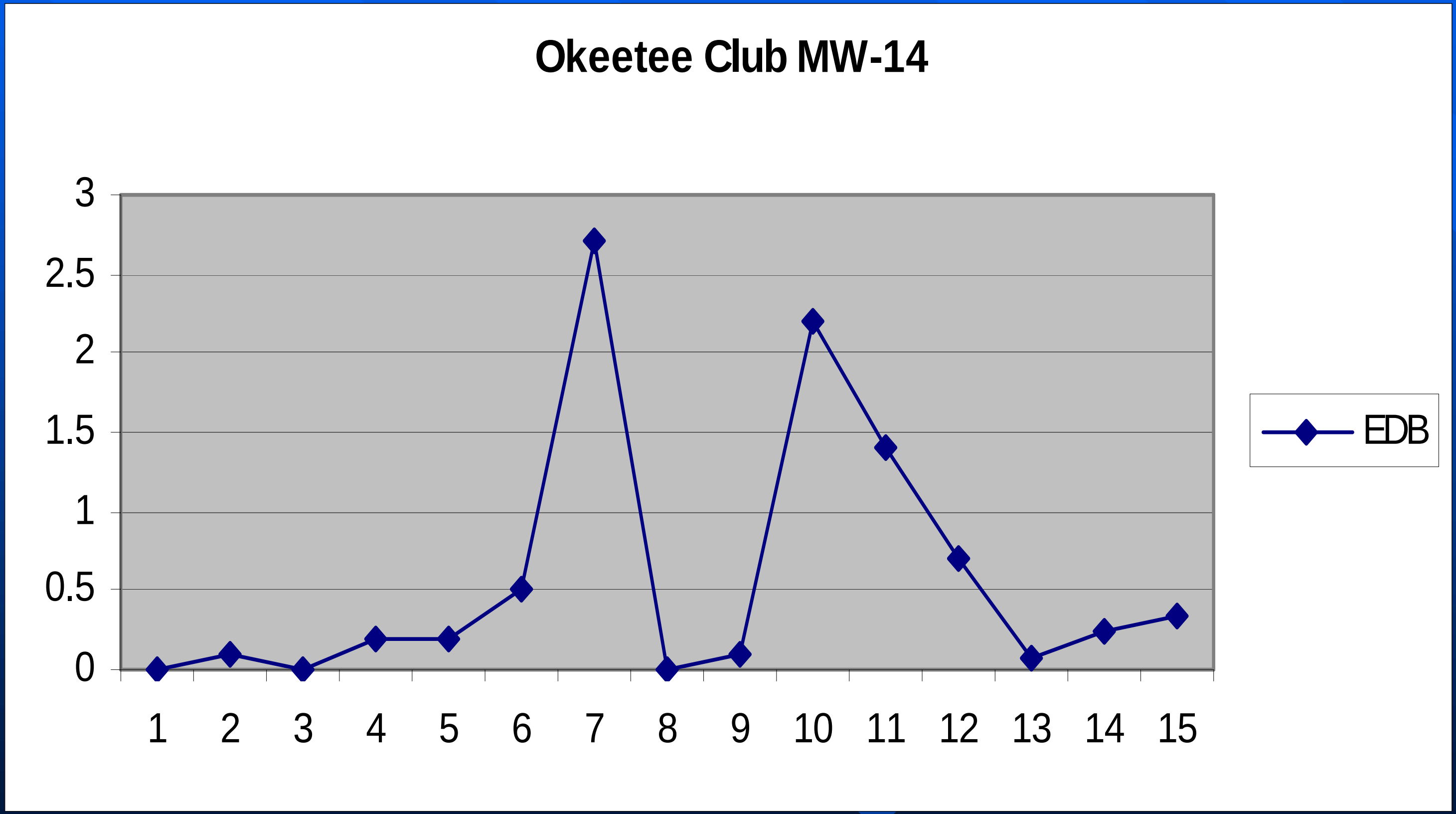
EDB near USTs



EDB 70' down-gradient



EDB 140’ Down-Gradient



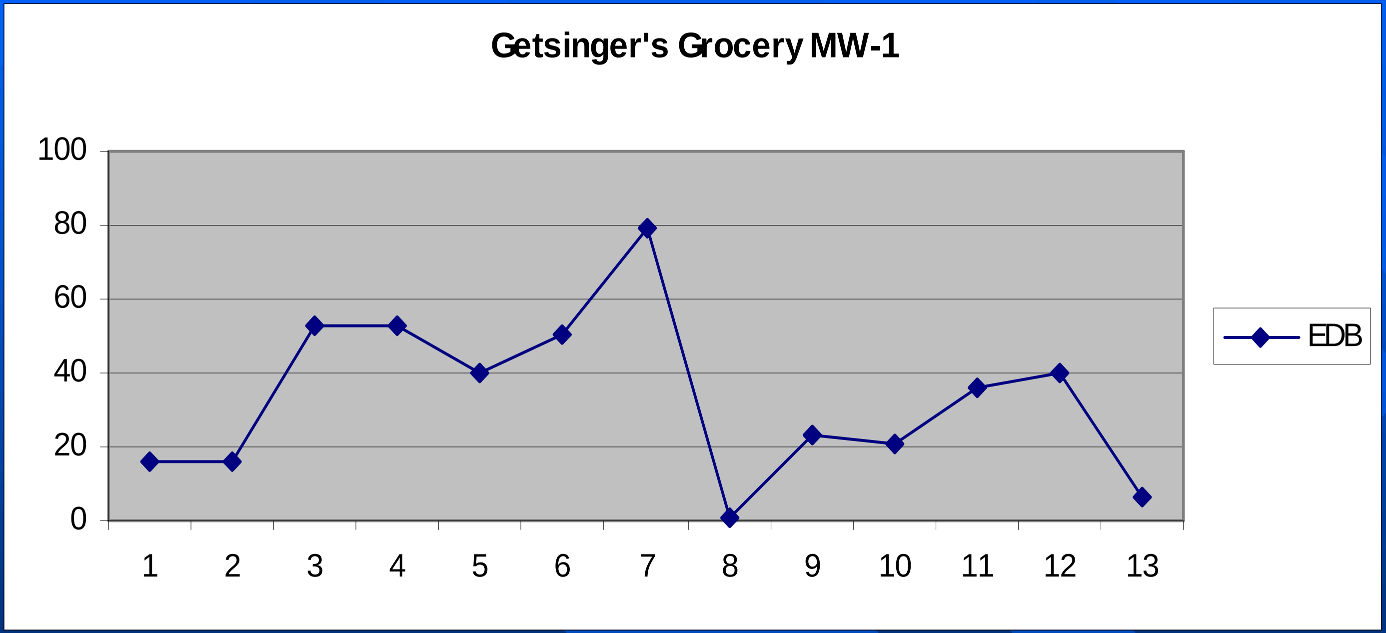
Theoretical

- EDB volatilized from residual drops of petroleum in soil – high vapor pressure
- EDB dissolves into soil moisture – low Koc and low Henry's Law Constant
- Soil moisture infiltrates down increasing EDB concentration in groundwater
- EDB migrates – low retardation coefficient
- Biodegradation slow compared to benzene

Chemical Oxidation

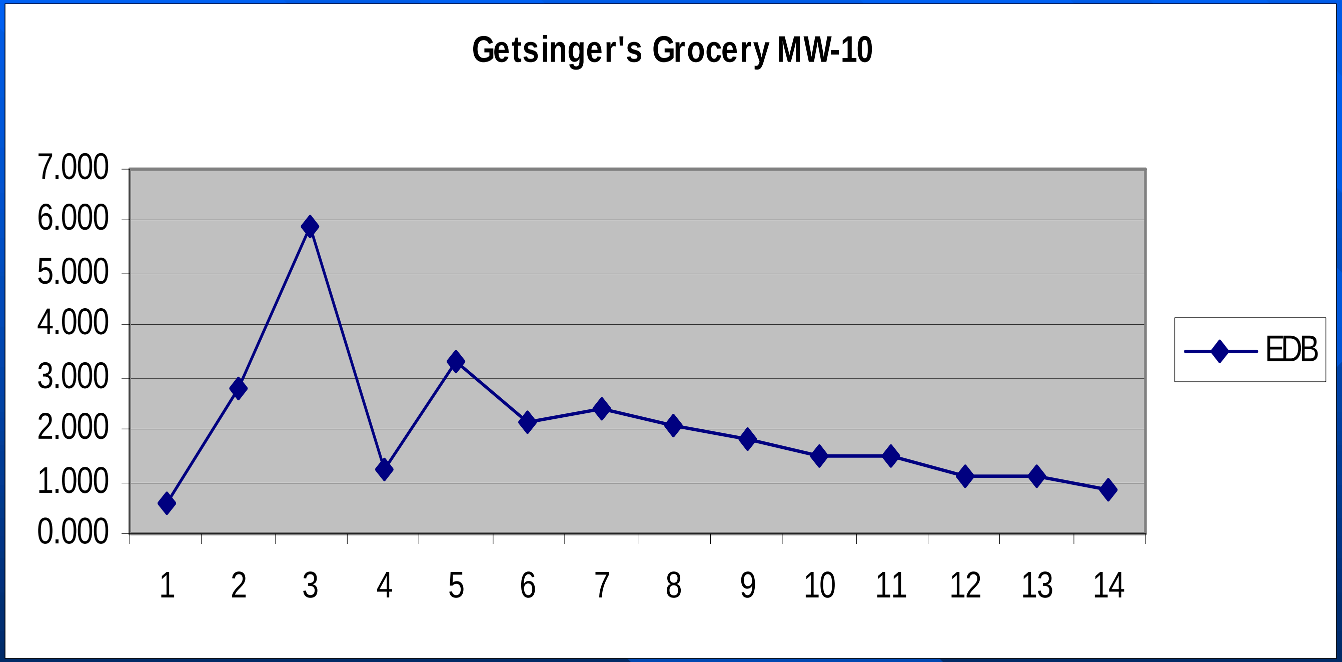
- Oxidant such as Hydrogen Peroxide (H_2O_2) is injected into the ground
- As the H_2O_2 contacts a chemical, the chemical is oxidized to form water and other by-products

EDB near USTs

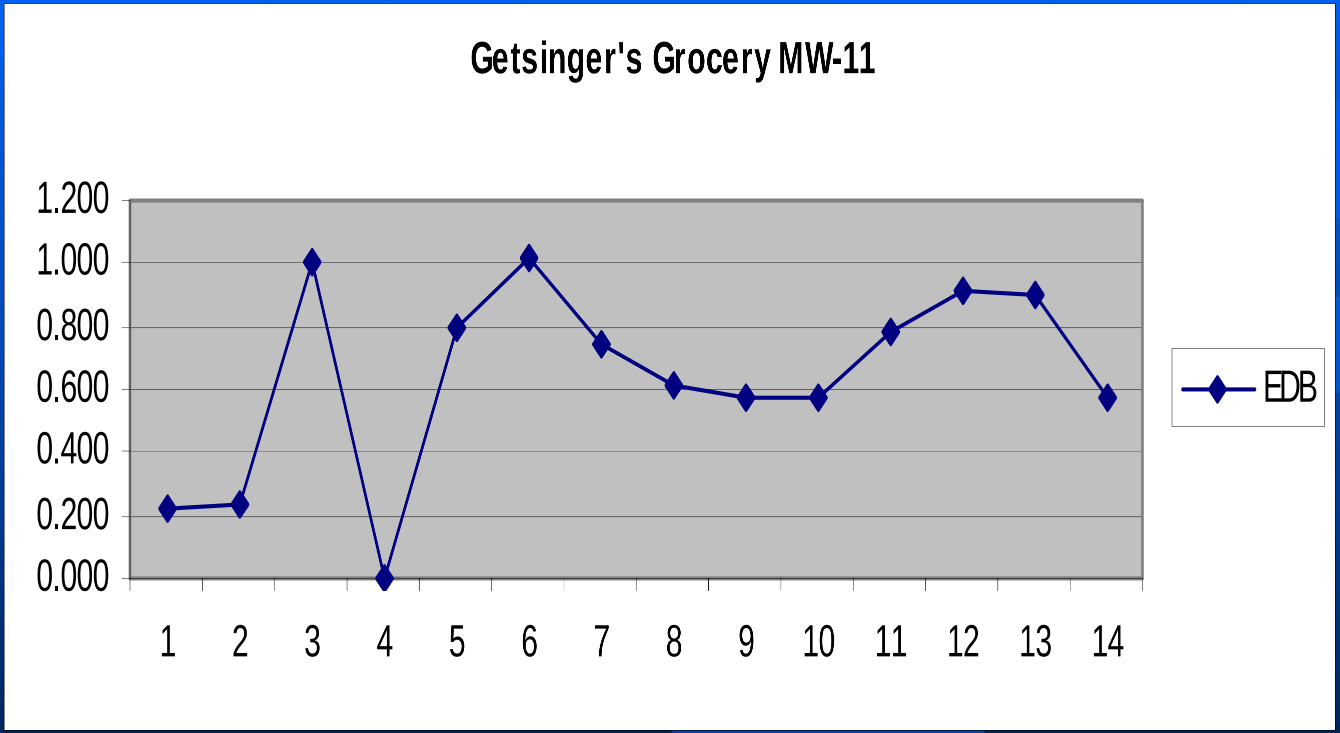


AFVR-2 & 5, ORC –6, H_2O_2-7 & 10, Bio-11, H_2O_2-12

EDB 60 feet down-gradient



EDB 110 feet down-gradient



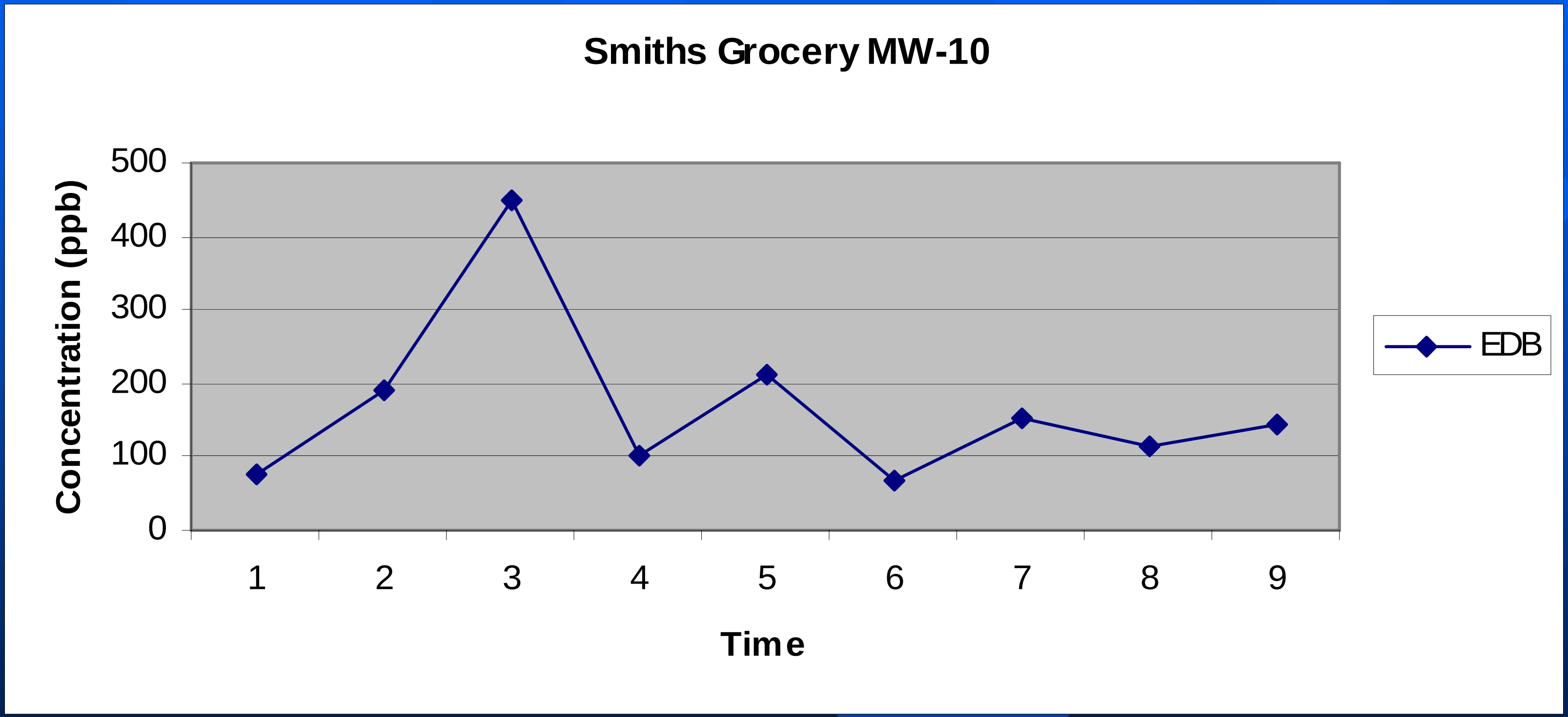
Chemical Oxidation

- H_2O_2 breaks down EDB but at a slower rate than benzene or MTBE
- The data suggests that EDB breakdown may be more efficient at higher H_2O_2 concentrations
- A large volume of H_2O_2, and/or more injection points may be necessary to prevent EDB remobilization

Bioremediation

- Injection of nutrients, oxygen, and sometimes microbes to enhance in-situ bioremediation
- Surfactants commonly used

Aerobic Bioremediation Example



Aerobic Bioremediation Observations

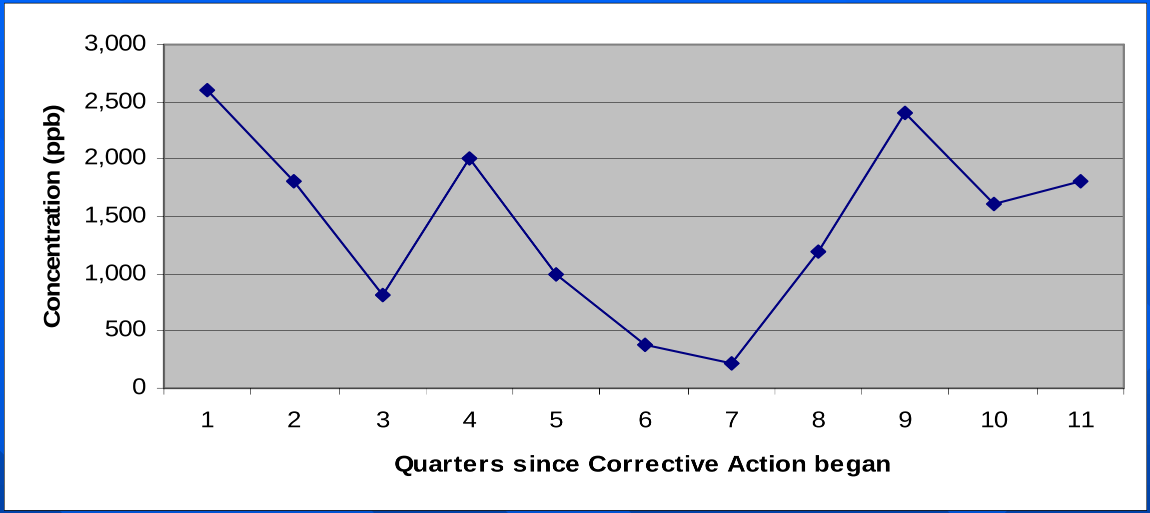
- EDB concentrations increase in source area after corrective action begins
- EDB reductions questionable
- EDB may be remobilized

PHOSter II™

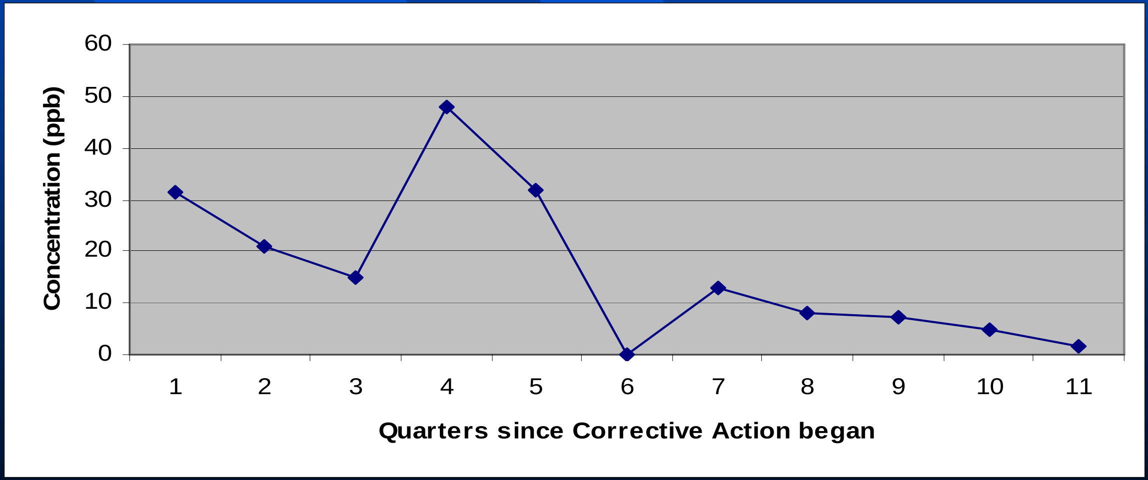
- Patented technology developed at Savannah River Site in South Carolina
- Vapor phase injection of air, nitrogen, and phosphorous

PHOSter II™ Example

Benzene



EDB



PHOSter II™ Observations

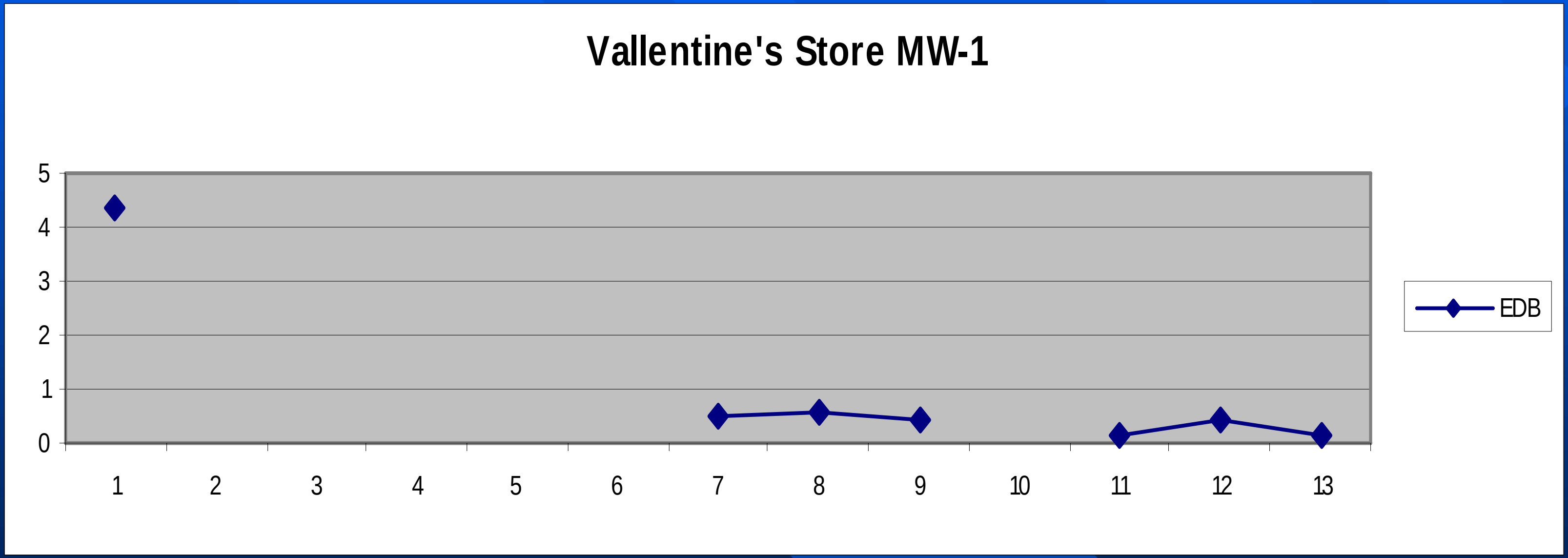
- Only one example
- EDB breakdown faster than BTEX ?
- More study of the PHOSter II™ technology relative to EDB remediation is recommended

Pump & Treat

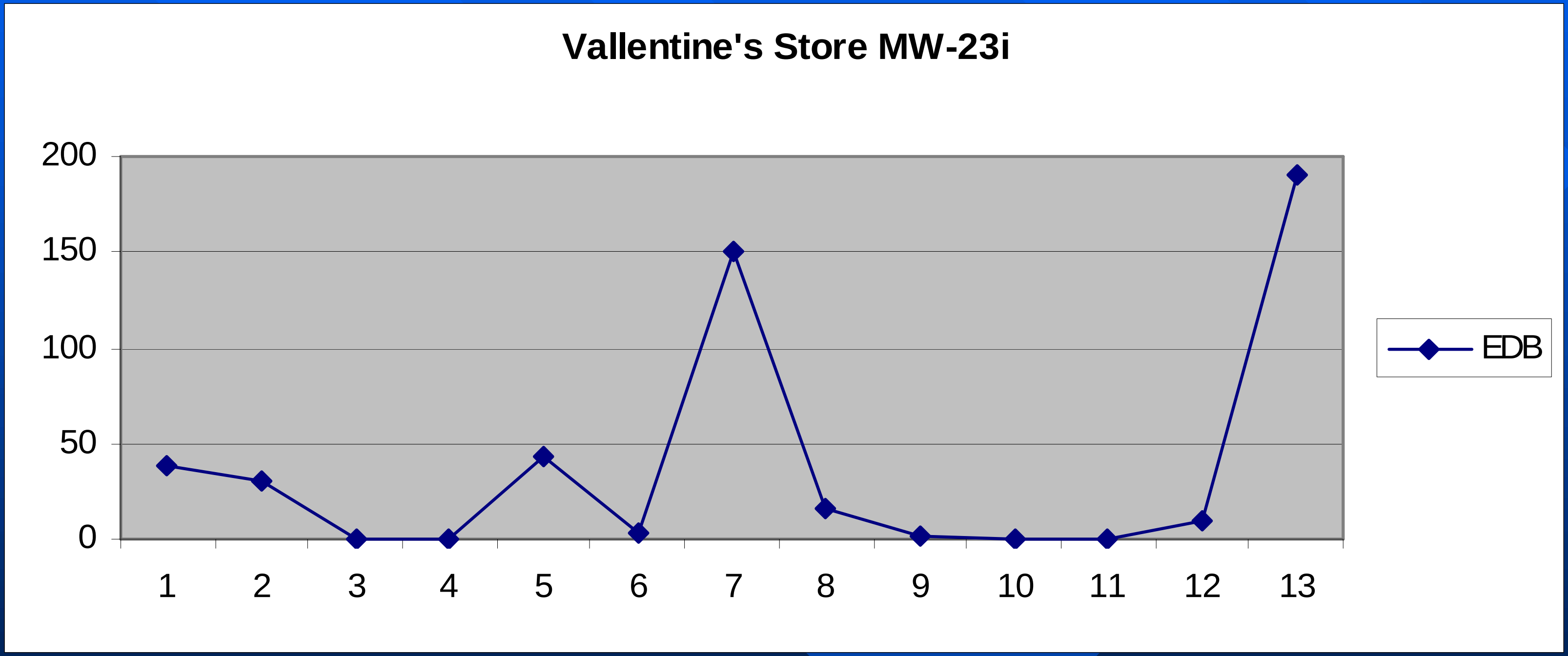
Recovered water run through an air stripper followed by an aerobic bio-reactor with microbes and nutrients followed by granular activated carbon

- Reductions from 1,200 ppb EDB to BDL observed in effluent
- Treated water is then re-injected

P&T Example – source area



P&T Example – 333 ft from source



Pump & Treat Observations

- Both Benzene and EDB show favorable decreases within radius of influence of pumping wells
- Outside of the radius of influence of the pumping wells, EDB may be re-mobilized

Conclusions-Continued

- EDB is present at ~ one-half of the assessed UST facilities in SC
- Because EDB behaves different than BTEX, different assessment strategies should be considered to avoid missing narrow and diving plumes

Conclusions-Continued

- Remediation of EDB is necessary in cases where existing or potential receptors are threatened

- EDB has different fate and transport properties than BTEX or MTBE

Conclusions - Continued

- The remedial strategy must be designed to also account for EDB’s properties and behavior
- The remedial strategy must be designed to preclude remobilization of EDB

Conclusions- continued

DO NOT ASSUME THAT A CORRECTIVE ACTION STRATEGY DESIGNED TO TREAT BTEX OR MTBE WILL ALSO WORK FOR EDB

Thank You for your attention!

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